

# **FLAME RETARDANT EPOXY RESINS**

C. M. Thompson\*, J. G. Smith Jr., J. W. Connell, P. M. Hergenrother  
National Aeronautics and Space Administration  
Langley Research Center  
Hampton, Virginia 23681-2199

and R. E. Lyon  
Federal Aviation Administration,  
Atlantic City International Airport, NJ, 08405

## **ABSTRACT**

As part of a program to develop fire resistant exterior composite structures for future subsonic commercial aircraft, flame retardant epoxy resins are under investigation. Epoxies and their curing agents (aromatic diamines) containing phosphorus were synthesized and used to prepare epoxy formulations. Phosphorus was incorporated within the backbone of the epoxy resin and not used as an additive. The resulting cured epoxies were characterized by thermogravimetric analysis, propane torch test, elemental analysis and microscale combustion calorimetry. Several formulations showed excellent flame retardation with phosphorous contents as low as 1.5% by weight. The fracture toughness of plaques of several cured formulations was determined on single-edge notched bend specimens. The chemistry and properties of these new epoxy formulations are discussed.

**KEY WORDS:** Fire Resistance, Structural Epoxy Resins, Phosphorus Containing Epoxies, Phosphorus Containing Diamines

## **1. INTRODUCTION**

The use of composite structures on both commercial and general aviation aircraft has been increasing primarily because of the advantages composites offer over metal (e.g. lower weight, better fatigue performance, no corrosion, better design flexibility, etc.). The new Airbus A380 is predicted to have more than 20% of the structural weight in composites. More than 50% of the structural weight of the new Boeing 7E7 is proposed to be composites, including for the first

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\* National Institute of Aerospace Staff Scientist, 144 Research Drive, Hampton, VA 23666

time, a composite fuselage. No fire resistance requirements currently exist for exterior composite structures on airplanes although work is underway to develop them. The primary concerns with aircraft fires are flame, smoke, and toxics. In a severe aircraft fire, smoke causes more loss in lives than heat or toxics. In a fire, carbon fiber composites release electrically conductive small carbon fibers that can cause considerable damage to electrical equipment and health problems (from ingestion). Fire resistant resin matrices in carbon fiber composites could significantly reduce the hazards resulting from an aircraft fire.

The use of phosphorus as a flame retardant, particularly in epoxy resins, has been widely studied and is the subject of recent review articles (1-2). A 3 year BRITE/EURAM Program was conducted in the European Community to develop new structural materials with improved fire resistance, reduced smoke and toxicity (3). This effort concentrated on the use of bis(3-aminophenyl)methyl phosphine oxide as a curing agent for epoxies (4). Several published articles evolved from this work (see ref. in 4, 5). Bis(3-aminophenyl)methylphosphine oxide was used previously as a curing agent for epoxies (6, 7). Phosphorus when incorporated in polymers is known to impart fire resistance through the formation of a char layer on the surface, which prevents oxygen from reaching the combustible material. Unlike halogenated fire retardant materials, phosphorus retards the spread of fire and minimizes the release of toxic gases (8). Phosphorus has been incorporated into polymeric materials both as an additive and as part of the polymeric chain. Additives are normally more economical but tend to leach out, retard processability and lower mechanical properties. Thus the focus of this work was to prepare and evaluate epoxy formulations containing phosphorus that can serve as composite resin matrices.

## 2. EXPERIMENTAL

**2.1 Materials** *N,N,N',N'*-Tetraglycidyl-4,4'-methylenedianiline (TGMDA), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (cycloaliphatic epoxy, Araldite CY 179), and 4,4'-sulfonyldianiline (DDS) were supplied by Applied Poleramic, Inc. Phosphorus oxychloride and triethylamine were purchased from a commercial source and distilled prior to use. All other chemicals were purchased from commercial sources and used without further purification.

**2.2 Characterization**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR Spectra were obtained on a Bruker 300 NMR Spectrometer. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer. Melting points were determined by DSC (heating rate of 10 °C/min, recorded at the onset and peak of the endotherm). Dynamic thermogravimetric analysis (TGA) was performed on a Seiko 200/220 instrument on cured formulations at a heating rate of 2.5 °C/min in nitrogen at a flow rate of 15 cm<sup>3</sup>/min. Epoxy equivalent weights were determined using the hydrogen bromide method (9). Elemental analyses were performed by Desert Analytics, Tucson, AZ. Liquid chromatography/mass spectroscopy (LC/MS) data was collected on a Waters 2695 Separations module interfaced with a Waters Integrity<sup>TM</sup> System Thermabeam Mass Detector.

### 2.3 Diamine Synthesis

**2.3.1 Synthesis of Bis(4-nitrophenyl)methylphosphonate** A 1L 3-neck round bottom flask fitted with a mechanical stirrer, an addition funnel, and a condenser was charged with 4-

nitrophenol (102.9 g, 0.74 mol), triethylamine (103 mL, 75 g, 0.74 mol), and tetrahydrofuran (THF, 250 mL). The solution was cooled with an ice-water bath. A solution of methylphosphonic dichloride (49 g, 0.37 mol) in 200 mL of THF was added dropwise over a period of 30 minutes. The reaction was stirred overnight and allowed to warm to room temperature. The reaction mixture was poured into 1 L of stirred water and the resulting precipitate was collected by vacuum filtration. The solid was dried in a vacuum oven at 55 °C for 4 h to give 103.86 g (83%) of tan crystalline solid, m.p. of 120-121.7 °C (lit. m.p. 121.5-122.5 °C) (10) by DSC. <sup>1</sup>H NMR (DMSO) ppm: [2.05, 2.22] (s, 3H, methyl), 7.49 (d, 4H), 8.27 (d, 4H). <sup>31</sup>P NMR (DMSO) ppm: 27.4. LC/MS: 1 peak, m/z = 337.

**2.3.2 Synthesis of Bis(4-aminophenyl)methylphosphonate 1** A large Parr<sup>TM</sup> bottle was charged with bis(4-nitrophenyl)methylphosphonate (40.32 g, 0.1192 mol), dry methanol (150 mL), and 5% Pd/C (0.2976 g). The bottle was shaken on a hydrogenator for 14 hrs under 40 psi of H<sub>2</sub>. The reaction was filtered to remove the catalyst and the filtrate was concentrated to give a yellow oil. The oil was covered with 150 mL of isopropanol and a pale yellow solid formed upon standing. The solid was collected and dried in a vacuum oven at 75 °C to give 28.6 g (86%), m.p. of 118-121 °C. <sup>1</sup>H NMR(DMSO) ppm: [1.60, 1.66] (s, 3H, methyl), 5.07 (s, 4H, amine), 6.49 (d, 4H), 6.81 (d, 4H). <sup>31</sup>P NMR (DMSO) ppm: 25.1. LC/MS: 1 peak, m/z = 277.

**2.3.3 Other Diamines** Bis(3-aminophenyl)methylphosphine oxide **2** (m.p. 148-151 °C. lit. m.p. 146-149 °C) (7), and bis(4-aminophenyl)phenylphosphine oxide **3** (m.p. 264-266 °C, lit. 264-265 °C) (11) were prepared following literature procedures.

**2.4 Epoxy Synthesis** Diglycidylmethylphosphonate **4** [epoxy equivalent weight (E.E.W.) 124, theoretical E.E.W. 104] was prepared following the procedure for diglycidylphenylphosphonate. Diglycidylphenylphosphonate **5** [E.E.W. 182, theoretical E.E.W 135] (Anal. Calcd. for C<sub>12</sub>H<sub>15</sub>O<sub>5</sub>P: C, 53.34; H, 5.60; P, 11.46. Found: C, 52.41; H, 5.30; P, 10.99) (12), triglycidylphosphite **6** (E.E.W. 212, theoretical E.E.W 83) (13), and triglycidylphosphate **7** (E.E.W. 117, theoretical E.E.W. 89) (14) were prepared following literature procedures.

**2.4.1 Synthesis of diglycidylmethylphosphonate 5** A 500 mL three-neck round bottom flask fitted with an addition funnel, a mechanical stirrer, and a condenser was charged with glycidol (28.14 g, 0.3762 mol), toluene (200 mL), and triethylamine (38.07 g, 0.3762 mol). The clear solution was cooled with an ice-water bath. A solution of methylphosphonic dichloride (23.73 g, 0.1785 mol) in toluene (100 mL) was added dropwise through the addition funnel. The reaction was stirred overnight and allowed to warm to room temperature. The reaction was filtered to remove triethylamine hydrochloride and the filter cake was washed with 100 mL of toluene. The filtrate was concentrated on a rotary evaporator to give a brown viscous liquid. The liquid was placed under high vacuum at 85 °C for 1h with stirring to remove toluene. (Yield 34.2 g, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) ppm: [1.45, 1.50] (3H, methyl group), [2.56, 2.74] (4H), 3.13 (2H), [3.81, 4.20] (4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm: [9.8, 10.2] (methyl), 44.0, 50.0, 65.8. <sup>31</sup>P NMR (CDCl<sub>3</sub>) ppm: 32.5. Anal. Calcd. for C<sub>7</sub>H<sub>13</sub>O<sub>5</sub>P: C, 40.39%; H, 6.30%; P, 14.88%. Found: C, 39.00%; H, 6.85%; P, 11.98%. (E.E.W. 124, theoretical E.E.W. 104).

**2.5 Cured Neat Resin Plaque Preparation** Epoxy compounds were combined with 80% stoichiometry of the curing agent at room temperature. The formulations were heated to and maintained at ~90 °C with periodic stirring for 30 min. The formulations were then degassed for 15-20 min in a vacuum oven at ~90 °C and subsequently cured for 4h at 100 °C followed by a 2h post-cure at 177 °C.

**2.6 Plane-Strain Fracture Toughness** Single-edge notched bend (SENB) specimens were prepared and tested following ASTM D 5045-99. Cured epoxy specimens having dimensions of approximately 1.27 cm x 6.35 cm x 0.64 cm thick were cut from a neat resin plaque. A crack was initiated with a razor blade (15) and the specimens were tested at a crosshead speed of 0.51 mm/min on a Korros Data test stand equipped with a 0.5 KN (45.5 kg) load cell. Three to five specimens were tested per resin formulation.

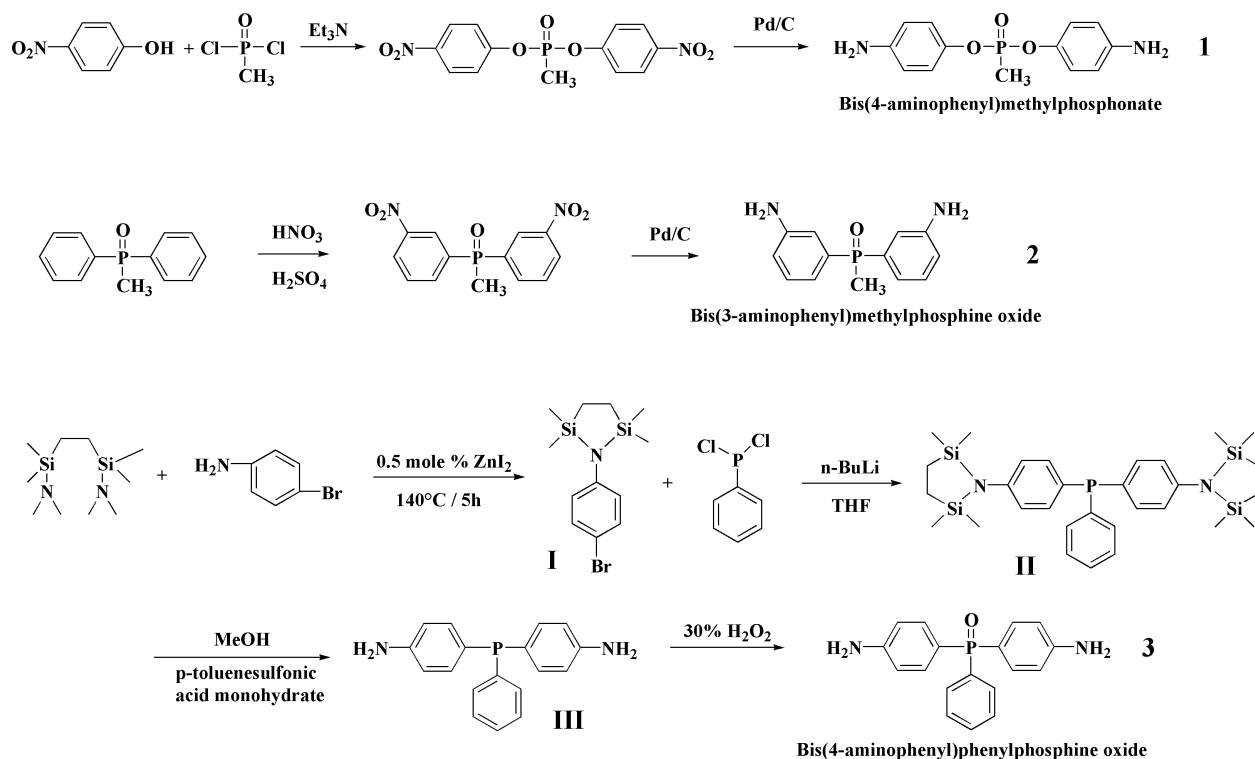
**2.7 Microscale Combustion Calorimetry** The specific heat release rate, total heat of combustion and char fraction were measured on cured epoxies using a pyrolysis combustion flow calorimeter (16-17). One to ten milligrams of sample were heated to 900 °C at a heating rate of 3.9 °C/s in a nitrogen atmosphere. The volatile, anaerobic thermal degradation products were mixed with oxygen prior to entering a 1000 °C combustion furnace. Three to five samples were tested per formulation.

### 3. RESULTS AND DISCUSSION

**3.1. Synthesis** The phosphorus-containing compounds in this study are known compounds and where possible, were prepared following literature procedures. The compounds were characterized with <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, LC/MS, elemental analysis, E.E.W. and melting point where applicable.

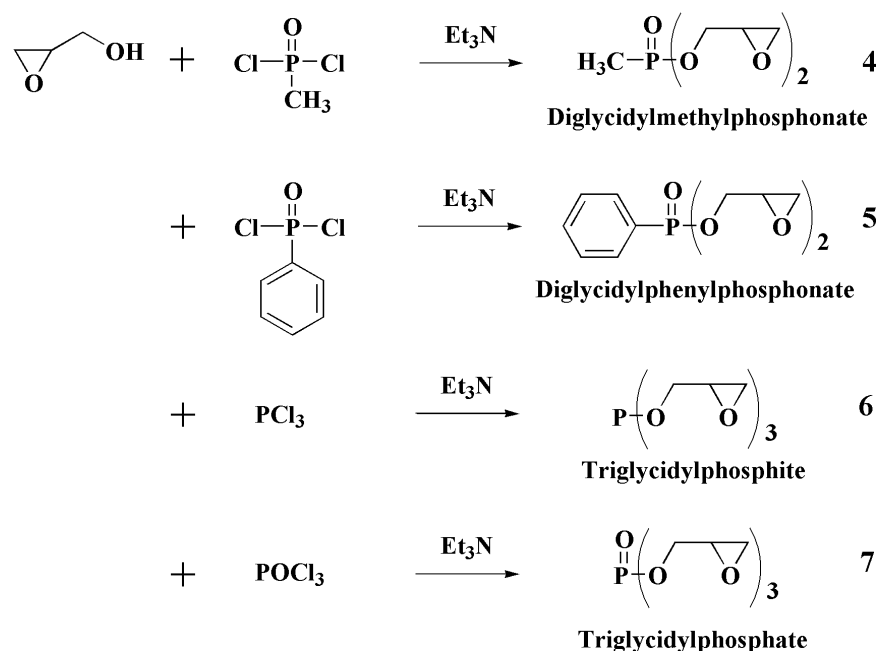
**3.1.1 Diamines** Reactions schemes for the synthesis of the phosphorus-containing diamines are shown in Scheme 1. Bis(4-aminophenyl)methylphosphonate **1** was prepared by reacting 4-nitrophenol with methylphosphonic dichloride to yield bis(4-nitrophenyl)methylphosphonate, that was subsequently reduced to diamine **1**. Likewise bis(3-aminophenyl)methylphosphine oxide **2** (7) was prepared through the nitration of diphenylmethylphosphine oxide followed by reduction of the dinitro compound to give diamine **2**.

Bis(4-aminophenyl)phenylphosphine oxide **3** (11) was prepared in 5 steps with an overall yield of 35%. First, 4-bromoaniline was protected with a STABASE group (1,1,4,4-tetramethyldisilylazacylopentyl) to give 1-bromo-4-(1,1,4,4-tetramethyldisilylazacylopentyl)benzene **I** in 70% overall purified yield (18). The protected bromoaniline was then reacted with dichlorophenylphosphine in the presence of n-butyl lithium/tetrahydrofuran to give phenylbis[4-(1,1,4,4-tetramethyldisilylazacylopentyl) phenyl]phosphine **II** in 71% yield (11). The STABASE protecting group was removed in methanol in the presence of p-toluenesulfonic acid monohydrate to give bis(4-aminophenyl)phenylphosphine **III** which was then oxidized with 30% hydrogen peroxide to give bis(4-aminophenyl)phenylphosphine oxide **3** in 75% yield (11).



**Scheme 1. Preparation of Diamines**

**3.1.2 Epoxies** The phosphorus-containing epoxy compounds **4-7** were prepared from the reaction of glycidol with the corresponding chloro phosphorus compound (methyl and phenyl phosphonic dichloride, phosphorus trichloride, and phosphorus oxychloride) in the presence of triethylamine as shown in Scheme 2. Epoxy equivalent weights, determined using the hydrogen bromide method, varied significantly from the theoretical values. This is common for epoxies because of impurities such as dimers, trimers, 1,2-glycols, etc. that are present.



**Scheme 2. Preparation of Epoxy Compounds**

**3.2 Cured Neat Resin Plaque Preparation** Epoxies were blended with 80% stoichiometry of the curing agent (diamine) at room temperature. The mixtures were heated to ~90 °C for 30-45 minutes with stirring, cured for 4 h at 100 °C and post-cured for 2 h at 177 °C. Except for formulations containing diamine **3**, transparent plaques were obtained. Elemental analysis was performed on cured formulations **F9**, **F11**, **F13**, and **F15** to verify the amount of phosphorus in the samples. The results are listed in Table 1 and showed good correlation for cured epoxies. For the samples tested, the % phosphorus found by elemental analysis was slightly lower than the amount calculated based on the weight of phosphorus containing epoxy used in the formulation.

**Table 1. Elemental Analysis on Select Cured Epoxy Formulations.**

Formulation		%C	%H	%N	%P
<b>F9</b>	Theoretical	64.84	6.37	7.66	1.01
	Found	64.25	6.13	7.73	0.87
<b>F11</b>	Theoretical	64.59	6.24	7.15	1.59
	Found	61.42	6.39	6.99	1.49
<b>F13</b>	Theoretical	62.36	6.33	6.36	1.65
	Found	60.54	6.48	6.29	1.57
<b>F15</b>	Theoretical	62.02	6.28	6.34	1.57
	Found	61.47	6.62	6.13	1.55

**3.3 Cured Epoxies From Phosphorus-Containing Diamines** Formulation **F1** was prepared from TGMMA cured with DDS and used as a standard to compare the properties of the phosphorus-containing epoxies. Initially the burn test consisted of placing a piece of the cured resin plaque in the flame of a propane torch for 5 seconds, removing it from the flame and noting the time for it to extinguish. As work progressed, the time in the propane torch flame was increased to 10 seconds. No noticeable difference was detected between 5 and 10 second burns with specimens from the same plaque. As presented in Table 2, formulation **F1** showed a sustained burn after removal from the propane torch flame. In formulations **F2-F4**, the DDS curing agent was completely replaced by phosphorus containing diamines **1-3** respectively to provide formulations having phosphorus contents (by weight) around 4.0 %. The cured plaques of formulations **F2** and **F3** were transparent, reddish-brown while **F4** was an opaque yellow. The viscosity of the uncured **F4** formulation was much higher than observed with the other formulations. Specimens **F2-F4** showed intumescence and little smoke in the propane torch flame and extinguished immediately after being removed from the propane torch flame. Formulation **F2** which contained diamine **1** gave a char yield of 31% at 800 °C in nitrogen, higher than those of formulations **F3** and **F4**.

**Table 2. General Properties of TGMMA Cured with Single Diamine**

Formulation	TGMMA, phr	Diamine, amount	% P	% Char at 800 °C, N <sub>2</sub> <sup>a</sup>	Flame Test <sup>b</sup>
<b>F1</b>	100	DDS, 48 phr	0	25	Sustained Burn
<b>F2</b>	100	<b>1</b> , 54 phr	3.9	31	Extinguished Immediately
<b>F3</b>	100	<b>2</b> , 47 phr	4.0	23	Extinguished Immediately
<b>F4</b>	100	<b>3</b> , 37 phr	3.7	24	Extinguished Immediately

a. TGA, 2.5 °C/min

b. Sample placed in propane torch flame for 5 seconds and removed.

Formulations **F5** and **F6** were prepared where part of the DDS was replaced with diamine **1** to reduce the amount of phosphorus in the cured epoxy specimens. This was done to determine the minimum phosphorus content necessary for the specimen to extinguish immediately after removal from the propane torch flame. As seen in Table 3, diamine **1** replaced 25% of the DDS in formulation **F1** to provide a phosphorus content of 0.9%. This specimen burned for approximately 2 seconds after removal from the propane torch flame. Diamine **1** replaced half of the DDS in formulation **F6** to provide a phosphorus content of 1.7%. The cured **F6** specimen extinguished immediately after removal from the flame. Char yields at 800 °C were the same (30-31%) for all formulations containing diamine **1**.

**Table 3. General Properties of TGMMA Cured with DDS/Diamine 1 Mixture<sup>a</sup>**

Formulation	DDS, %	Diamine 1, %	% P	% Char at 800 °C, N <sub>2</sub> <sup>b</sup>	Flame Test <sup>c</sup>
<b>F1</b>	100	0	0	25	Sustained Burn

<b>F5</b>	75	25	0.9	30	2 Second Burn
<b>F6</b>	50	50	1.7	31	Extinguished Immediately
<b>F2</b>	0	100	3.9	31	Extinguished Immediately

a. Total amount of curing agent was 80% of stoichiometry

b. TGA, 2.5 °C/min

c. Sample placed in propane torch flame for 5 seconds

Microscale combustion calorimetry analysis was performed on cured formulations **F1-F3** to obtain the heat release capacity (HRC) and total heat release. Typically HRC values below 300 J/g-K are self extinguishing in vertical Bunsen burner tests of ignition resistance. HRC values below 120 J/g-K typically pass the FAA heat release rate test for aircraft cabin materials. As presented in Table 4, formulation **F1** containing no phosphorus had a high HRC which coincided with the sustained burn observed with the propane torch flame test. Formulation **F2** had a lower HRC and total heat release than measured for formulation **F3**. The HRC of 356 J/g-K measured for **F3** suggested that this sample would not self extinguish, but it extinguished immediately after removal from the propane torch flame test. Microscale combustion calorimetry was not done on **F4** because a good quality specimen could not be obtained.

**Table 4. Microscale Combustion Calorimetry of TGMDA Cured with Phosphorus-Containing Diamines**

Formulation	%P	HR Capacity (J/g-K)	Total HR (kJ/g)
<b>F1</b>	0	405	20.5
<b>F2</b>	3.9	225	15.5
<b>F3</b>	4.0	356	21.1

**3.4 Cured Epoxies from Phosphorus-Containing Epoxy Compound** Epoxy formulations were also prepared where phosphorus was introduced via epoxy compounds. These formulations were prepared using only DDS as the curing agent. Formulations **F7-F9** contained diglycidylmethylphosphonate **4** in amounts ranging from 10 to 33 phr as shown in Table 5. These specimens have phosphorus contents ranging from 1 to 3.3% and all extinguished immediately upon removal from the propane torch flame. The three specimens also showed good intumescence and low smoke. A char yield of 35% at 800 °C was obtained by TGA for specimen **F7**.

**Table 5. General Properties of Formulations From Diglycidylmethylphosphonate<sup>a</sup>**

Formulation	TGMDA, phr	$\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{O}}{\text{P}}}(\text{O}-\text{CH}_2-\text{CH}_2-\text{O})_2$ , phr	%P	% Char at 800 °C, N <sub>2</sub> <sup>b</sup>	Flame Test <sup>c</sup>
<b>F7</b>	67	33	3.3	35	Extinguished Immediately
<b>F8</b>	80	20	2.1	28	Extinguished Immediately

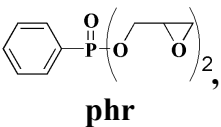


<b>F9</b>	90	10	0.87 <sup>d</sup>	31	Extinguished Immediately
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**a.** Cured with 80% stoichiometric amount of DDS  
**b.** TGA, 2.5 °C/min  
**c.** Sample placed in propane torch flame for 10 seconds  
**d.** Result from Elemental Analysis

Formulations **F10-F12** were prepared using diglycidylphenylphosphonate **5** in concentrations ranging from 40-10 phr. As shown in Table 6, **F10** and **F11** with 3.2% and 1.6% phosphorus content respectively both extinguished immediately upon removal from the propane torch flame and exhibited good intumescence and low smoke. Formulation **F12** with 0.8 % phosphorus burned for approximately 2 seconds upon removal from the flame but showed good intumescence. As seen with previous specimens, phosphorus content of 1-1.5% appeared to be necessary to obtain acceptable fire retardation. Char yields at 800 °C by TGA for **F10-F12** ranged from 33-36%.

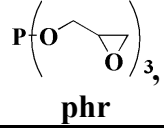
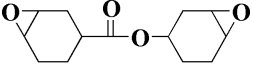
**Table 6. General Properties of Formulations From Diglycidylphenylphosphonate<sup>a</sup>**

Formulation	TGMDA, phr	 phr	%P	% Char at 800 °C, N <sub>2</sub> <sup>b</sup>	Flame Test <sup>c</sup>
<b>F10</b>	60	40	3.2	36	Extinguished Immediately
<b>F11</b>	80	20	1.5 <sup>d</sup>	34	Extinguished Immediately
<b>F12</b>	90	10	0.8	33	2 second burn

- a.** Cured with 80% stoichiometric amount of DDS  
**b.** TGA, 2.5 °C/min  
**c.** Sample placed in propane torch flame for 10 seconds.  
**d.** Result from Elemental Analysis

Triglycidyl epoxies **6** and **7** were also evaluated in cured epoxy formulations. A cycloaliphatic epoxy at a concentration of 20 phr was used as a partial replacement for TGMDA in **F13-F16**. This diepoxy was used to help solubilize the DDS but it is also used in epoxy formulations (generally with boron trifluoride) to improve handleability (tack and outtime). General properties are shown in Tables 7 and 8.

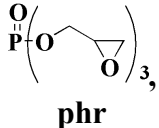
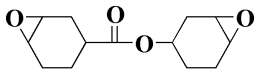
**Table 7. General Properties of Formulations From Triglycidylphosphite<sup>a</sup>**

Formulation	TGMDA, phr	 phr		%P	% Char at 800 °C, N <sub>2</sub> <sup>b</sup>	Flame Test <sup>c</sup>
<b>F13</b>	60	20	20	1.56 <sup>d</sup>	35	Extinguished Immediately
<b>F14</b>	60	10	20	0.9	-	~1 second burn

- a. Cured with 80% stoichiometric amount of DDS
- b. TGA, 2.5 °C/min
- c. Sample placed in propane torch flame for 10 seconds
- d. Result from Elemental Analysis

Triglycidylphosphite **6** appeared to be more reactive than the other epoxies and a small amount of gel was observed during the mixing and curing of the epoxy formulation. Formulation **F13** containing 1.6% phosphorus extinguished immediately after removal from the propane torch flame and showed good intumescence and low smoke. **F14**, which contained less than 1% phosphorus, burned for 1 second upon removal from the propane torch flame with moderate intumescence. The char yield of **F13** at 800 °C by TGA was 35%.

**Table 8. General Properties of Formulation From Triglycidylphosphate<sup>a</sup>**

Formulation	TGMDA, phr	 phr		%P	% Char at 800 °C, N <sub>2</sub> <sup>b</sup>	Flame Test <sup>c</sup>
<b>F15</b>	60	20	20	1.55 <sup>d</sup>	38	Extinguished Immediately
<b>F16</b>	60	10	20	0.9	-	~1 second burn

- a. Cured with 80% stoichiometric amount of DDS
- b. TGA, 2.5 °C/min
- c. Sample placed in propane torch flame for 10 seconds
- d. Result from Elemental Analysis

Formulation **F15** also contained 1.6% phosphorus and extinguished immediately upon removal from the propane torch flame. The char yield at 800 °C of 38% was slightly higher than that of **F13**. Formulation **F16** contained slightly less than 1% phosphorus and burned for approximately 1 second after removal from the propane torch flame.

Several formulations incorporating the phosphorus-containing epoxies were analyzed using microscale combustion calorimetry. Reproducibility varied in samples **F8**, **F9**, and **F15** with the highest standard deviation of 33% when 4 specimens were tested from the same sample, suggesting non-homogeneity. The HRC values in Table 9 for these samples represent averages of the 4 test specimens. The other samples in Table 9 showed good reproducibility with standard deviation of < 5%. The fire resistance performance of these materials was better than that observed for materials incorporating phosphorus-containing diamines. Formulations **F7** and **F10** with approximately 3.3% phosphorus had significantly lower HRCs of 108 and 113 J/g-K respectively compared to **F2** with 3.9 % phosphorus and a HRC of 225 J/g-K. Formulations **F7-F9** from diglycidylmethylphosphonate **4** showed HRC increase from 108 to 179 J/g-K as the phosphorus content decreased from 3.3 to 0.9%. A similar trend was observed with formulations **F10-F12**, made with diglycidylphenylphosphonate **5**. Higher phosphorus content generally provided lower HRC values.

**Table 9. Microscale Combustion Calorimetry of Formulations Incorporating Phosphorus-Containing Epoxy Compounds**

Formulation	%P	HR Capacity (J/g-K)	Total HR (kJ/g)
<b>F7</b>	3.3	108	14.6
<b>F8</b>	2.1	128	14.2
<b>F9</b>	0.9	179	15.3
<b>F10</b>	3.2	113	13.9
<b>F11</b>	1.5	119	16.1
<b>F12</b>	0.8	135	16.1
<b>F13</b>	1.6	138	14.9
<b>F15</b>	1.6	202	14.7

**3.5 Plane-Strain Fracture Toughness Measurements** Single-edge notched bend (SENB) specimens were prepared and tested for formulations **F1**, **F2**, **F8**, **F11**, and **F15** to evaluate the effect of incorporating the phosphorus-containing compounds into epoxy resins. Since the formulations are not toughened, the measured values were not expected to be high. As shown in Table 10, the fracture toughness values ranged from 0.54 to 0.79 MPa m<sup>1/2</sup>. The values obtained for formulations **F2**, **F8**, **F11**, and **F15** were essentially the same as measured for **F1** (TGMDA/DDS). Incorporating the phosphorus containing compounds into the TGMDA formulations had no effect on the fracture toughness of the cured epoxies.

**Table 10. Plane-Strain Fracture Toughness**

Formulation	Fracture Toughness, MPa m <sup>1/2</sup> ± 1 std. dev.
<b>F1</b>	0.62 ± 0.04
<b>F2</b>	0.68 ± 0.04
<b>F8</b>	0.79 ± 0.05
<b>F11</b>	0.64 ± 0.13
<b>F15</b>	0.54 ± 0.05

## 4. SUMMARY

Phosphorus-containing epoxy formulations were studied as part of a program to develop technology leading to fire resistant structural resins. Phosphorus was introduced as either part of the diamine curing agent or part of an epoxy compound. Good fire retardation was obtained from incorporating as little as 1.5% phosphorus. Microscale combustion calorimetry showed that formulations from the phosphorus-containing epoxies performed better than those from the phosphorus-containing diamines at similar loading levels.

The use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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## 6. REFERENCES

1. S-Y. Lu and I. Hamerton, Prog. Polym. Sci., **27**, 1661 (2002) and references therein.
2. E.D. Weil and S. Levchik, J. Fire Science, **22**(1), 25 (2004) and references therein.
3. M. Costes and M. Henry, Report Reference Number:DCR/M-60606/F3-94, Aerospatiale Suresnes DCR/MC, March 21, 1995
4. S.V. Levchik, G. Camino, L. Costa, and M.P. Luda, Poly. Degrad. Stab., **54**, 317 (1996) (also please see pages 305, 311, and 329 in this journal issue).
5. S. V. Levchik, G. Camino, M. P. Luda, L. Costa, G. Muller, B. Costes, and Y. Henry, Polymers for Adv. Tech., **7**, 823 (1996)
6. D. A. Kourtides, J. A. Parker, T. W. Gaints, N. Bilow, and M. Hsu, in Proceedings of the Adhesives for Industry Conference, El Segundo, CA, June 24-25, 1980
7. I.K. Varma and U. Gupta, J. Macromol. Sci.-Chem., **A23**(1), 19 (1986).
8. K. Kampke-Thiel, D. Lenoir, A. Kettrup, E. Herdtweck, D. Gleich, and W. R. Thiel, Chem. Eur. J., **4**(8), 1581 (1998)
9. H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw-Hill, Inc. New York, 1967, p. 4-17.
10. P. Blumbergs, C.B. Thanawalla, and A.B. Ash, J. Org Chem, **36**(14), 2023 (1971).
11. C.M. Whitaker, K.L. Kott, and R.J. McMahon, J. Org. Chem., **60**, 3499 (1995).
12. Y.-L. Liu, G.-H. Hsiue, Y.-S. Chiu, R.-J. Jeng, and L.-H. Perng, J. Appl. Polym. Sci., **61**, 613 (1996).
13. U.S. Pat. 2,856,369 (Oct. 14, 1958) C.W. Smith, G.B. Payne, and E.C. Shokal (to the Shell Development Company).
14. U.S. Pat. 2,826,592 (March 11, 1958) A.C. Mueller, C.W. Schroeder, and E.C. Shokal (to the Shell Development Company)
15. D.A. Dillard, P.R. McDaniels, and J.A. Hinkley, J. Materials Science Letters, **12**, 1258 (1993).
16. R.E. Lyon and R.N. Walters, Presented at the 9<sup>th</sup> Annual BCC Conference on Flame Retardancy of Polymeric Materials, Stamford, CT, June 1-3, 1998.
17. R.E. Lyon, U.S. Pat. 6,464,391 (Oct. 15, 2002) (to the United States of America as represented by the Secretary of Transportation)
18. T.L. Guggenheim, Tetrahedron Letters, **25** (12), 153 (1984).

## 7. BIOGRAPHIES

Craig M. Thompson is a staff scientist with the National Institute of Aerospace (NIA) working in the Advanced Materials and Processing Branch (AMPB) of the Structures and Materials Competency (SMC) at NASA Langley Research Center (LaRC). Prior to joining the NIA he was a National Research Council Research Associate at NASA LaRC. He received a B.S. degree from The University of Michigan in 1991 and a Ph.D. in Polymer Chemistry from Rensselaer Polytechnic Institute in 1999. His work has focused on the development of high performance polymers for aerospace applications.

Joseph G. Smith, Jr. is a senior polymer scientist in the AMPB of the Structures and Materials Competency (SMC) at NASA LaRC. He received a B.S. degree from High Point College in 1985 and a Ph.D. from Virginia Commonwealth University in 1990. Prior to joining NASA LaRC in September 1994, he held postdoctoral research positions with the University of Akron and Virginia Commonwealth University. His work at NASA has focused on the development of high performance polymers for aerospace applications.

John W. Connell is a senior polymer scientist in the AMPB of the SMC at NASA LaRC. He received B.S. and Ph. D. degrees from Virginia Commonwealth University in 1982 and 1986, respectively. Prior to joining NASA LaRC in January 1988, he was a research associate at Virginia Commonwealth University. Since coming to NASA, his work has focused on the development of high performance polymers for aerospace applications.

Paul M. Hergenrother is a senior polymer scientist in the AMPB of the SMC at NASA LaRC. He received a B.S. degree from Geneva College and took graduate work at the University of Pittsburgh and Carnegie-Mellon University. Prior to joining NASA he held various research and management positions at the Koppers Co., The Boeing Co., Whittaker Corp. and Virginia Polytechnic Institute and State University. His work at NASA has focused on the development of high performance polymers for aerospace applications.